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LOCAL DEFECT ARRAYS IN OXIDES.(U)
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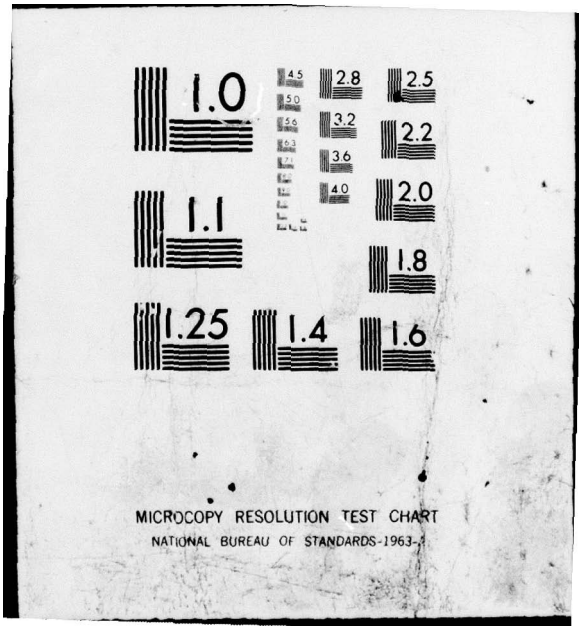
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SUMMARY

The goals of this grant were three-fold:

1) To develop quantitative techniques for the analysis of the diffuse x-ray scattering from oxides. While such studies of local atomic arrangements have been possible for some time with binary alloys, this has not been the case for oxides, despite the fact that there is considerable interest in the local defect arrangements in non-stoichiometric oxides (because of their possible connection to the properties of such oxides). The reasons for this state of affairs is that these oxides are ternary systems, involving anions, cations and vacancies. The diffuse scattering is a function of many (often overlapping) interionic pair probabilities. Also, the complex unit cell of these materials seems to require measurements in a prohibitively large volume of reciprocal space.

2) The monoxides of the first transition series of elements have a unique variation in properties. They are metallic conductors for the low atomic number end of the series, but semiconductors for the high atomic numbers. Is there a link between the defect arrangement and this behavior?

3) To clarify the defect arrays in stabilized zirconia.

The studies ~~during this three year grant~~ have concentrated on $VO_2^{\square}$, $VO_x^{\square}$, $TiO_x^{\square}$, $Zr(Ca)O_{2-x}^{\square}$ and $Zr(Y)O_{2-x}^{\square}$. Our results can be summarized as follows:

1) It is possible to successfully separate the effects of atomic displacements and ionic arrangements in the diffuse scattering from oxide single crystals. This can be done with data in a restricted volume in reciprocal space, by least-squares procedures.

2) The diffuse scattering in VO_x (vs x) and in VO_2 has been shown to be closely linked to the Fermi surface of these materials. Suggestions by Amelinckx and co-workers that this scattering can be described as due to local ionic arrangements on the basic octahedron of the structure have been shown to be incorrect.

3) Ordered (monoclinic) TiO_x has waves of Ti and O ion vancancies every third (100) plane in the [010] direction, the amplitude being considerably larger for the Ti ions than for the O. There are no tetrahedrally co-ordinated ("interstitial") ions. The ordering process of these vancancies has been shown to be first order, and caused to be so by the effect of distortion on the vacancy-vacancy and vacancy-electron interaction energies, i.e. by a vacancy-strain coupling.

4) In cubic disordered TiO_x, vacancy interactions extend out to sixth neighbors. (In this study it was also shown how to measure the interaction energies.) The short-range order parameters between vacancies, cations and anions were measured at 1323°K, the first such study of a complex oxide at high temperatures. The local ionic arrangements in this disordered state closely resemble those in the ordered phase. (See (3) above.)

A considerable contribution to the conductivity of this metallic oxide was suggested due to local order.

5) In VO_x there are tetrahedrally coordinated V ions, as well as vacancies on the cation and anion octrahedral sites. For $X > 1$, this material is a semiconductor, and we have found that the defect array is a cluster much like the Koch-Cohen cluster in Fe_xO. This is a vacancy cluster, occluding a few interstitial cations. But for $X < 1$ it is metallic like TiO_x, and we find that the point defects are arranged in sheets, much as they are in TiO_x. Thus there are clearly long-range interactions controlling both the defect arrangement and the conductivity.

6) Direct evidence has been obtained of excess electron density at cation-vacancies. While it has long been postulated that such sites are charged, this is the first direct evidence that such charge actually exists.

7) The ionic displacements around defects in VO_x are clearly also controlled by long-range effects, not Jahn-Teller interactions.

8) In stabilized zirconias, stabilizing elements such as Ca & Zr introduce O vacancies for charge compensation. But there are conflicting reports in the literature of the nature and direction of the shifts of ions around these vacancies. We have now found that these are in ⟨100⟩ directions and of the same magnitude as those in the cubic-tetragonal transition in pure zirconia. We have also found that the stabilizing ions are first-neighbor to vacancies probably both to reduce the distortion of the larger solute ions, and for charge compensation. We speculate that the retention of the cubic phase caused by solutes like Ca or Y are due to a) the increased entropy of solute and vacancies b) the dispersal of the displacements by the solute - that is the trapping of phonons.

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Studies are described of the extended defects in VO_x, TiO_x and stabilized zirconias with diffuse x-ray scattering.

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